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Mineralogy and Geochemistry of Residual Clay Occurrences in Idi-Ayunre and Akure Areas, Southwestern Nigeria

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Abstract

Three residual clay occurrences in Idi-Ayunre, and Akure areas which belong to the Precambrian basement complex of southwestern Nigeria were investigated for their mineralogical, chemical and industrial properties. The investigation was to evaluate their industrial applications and economic importance. The clay within the weathered profiles above banded gneiss at Idi-Ayunre is whitish with red spots, whereas the clays derived from profiles above porphyritic granite and granite gneiss in Akure are grayish and brown in color respectively.

The X-ray diffraction studies show that kaolinite is the dominant clay mineral, goethite, microcline, quartz, albite are the major non clay minerals in the samples. Chemical data showed that the average values of SiO_2, Al_2O_3, and Fe_2O_3 were 52.3. 30.29 and 3.54 wt% respectively constituting 86.13% of the bulk compositions.

Evaluation of the clay thermal characteristic, firing colour, water absorption capacities and shrinkage values show that the brownish Idi-Ayunre clay, gray and brown Akure kaolinitic clays could serve as raw materials for ceramics, building bricks, and other structural wares

Keywords: clays, Nigeria, laterite, kaolinite, ceramics

1. Introduction

Laterites are most widely distributed soils in southwestern Nigeria which is characterized by tropical climate. Laterites and lateritic clays are commonly used as fillers, additives and extenders in construction, ceramic, paint, paper, pharmaceutical, agriculture and refractory industries. (Elueze 1993, Bolarinwa, 2009).

The Precambrian basement complex of southwestern Nigeria consists predominantly of gneisses, schists and quartzites, which granitic and basic intrusive have been emplaced. Some of the basement rocks have been greatly weathered to form residual clays in the southwestern Nigeria, extensive occurrences and utilization of such residual bodies have been reported by various scientists. Based on the evaluation of the chemical compositions, thermal properties and colour, the residual clays in Abeokuta area are of great economic importance according to Bolarinwa (1992). Elueze and Bolarinwa (1995). presented the industrial applications of some of the clay deposits in southwestern Nigeriae clay deposit. Aribisala concluded that some of the clay deposits in Nigeria could be used as raw materials in the building and constructional sectors. . Emofurieta et al., (1995) described the mineralogy and the geochemistry of lateritic clays derived from weathered biotite gneiss in Ile-Ife. Southwestern Nigeria. They observed that the clay assemblage is dominated by kaolinite, Montmorilonite, vermiculite and illite. Two lateritic profiles on ultramafic rocks of southwestern Nigeria were investigated for the formation of secondary minerals by Ige et al. 2005.

Recent geological investigations revealed that quite a number of the residual and sedimentary clay bodies which could be economically viable have not been adequately assessed and utilized. With the increase in population, there is need for provision of jobs, building bricks, houses, and household equipments. The present study is therefore necessary to evaluate the residual clay bodies in Idi-ayunre and Akure areas, southwestern Nigeria and also to serve as scientific contribution towards increasing the local raw material for industries.

2. Geological Settings

Idi-Ayunre is underlain by banded gneiss and granite gneiss whereas Akure consists predominantly of porphyritic granite, charnockite and undifferentiated migmatite gneiss (Oyinloye 2007). The minor rock types are vein quartz and pegmatite. They occur as intrusions in the major rock types. Banded gneiss stretches through Idi Ayunre and its environs (Figure 2). Banded gneiss is grey in colour and texturally medium grained. It consists of quartz, plagioclase feldspar and biotite. Banded gneiss is strongly foliated and the foliation is expressed by alternation of mafic layers which contain mostly biotite with the felsic layer made up of quartz and feldspar .The rock is highly susceptible to weathering due to its plane of weakness. The Northeastern part consists predominantly of granite gneiss and mineralogically consists of plagioclase feldspar, quartz, biotite and hornblende.

In Akure area, porphyritic granite, which is the second abundant rock type in the region, covers the entire eastern part, stretching through the northern region and covering part of the western region (Figure3) However, it occurs mostly as massive outcrops. The colour is grey and medium grained. The phenocryst is made of feldspartic minerals embed in the matrix of feldspar and quartz. Mineralogically, Porphyritic granite contains both felsic and mafic minerals. The felsic minerals consist of feldspar and quartz, whereas the mafic mineral consists of biotite and other accessory minerals. The mafic are randomly distributed within the felsic minerals. The migmatite found in this area is located at the central part of Akure. They range from coarsely mixed gneisses to diffuse textured rocks of variable grain size. Migmatite consists of leucocratic component which alternate with basic component. The leucocratic component ranges from fine-grained granitic gneisses to medium grained banded gneisses especially around Shagari estate, Akure. Quartz and pegmatite veins cut across migmatite discordantly indicating that they are younger than the migmatite .The main component minerals are quartz, plagioclase, and biotite. Pegmatite occurs and quartz vein as intrusions in nearly all the various rock types. They cut across the different rocks concordantly or discordantly and sometimes occupy the joint spaces.

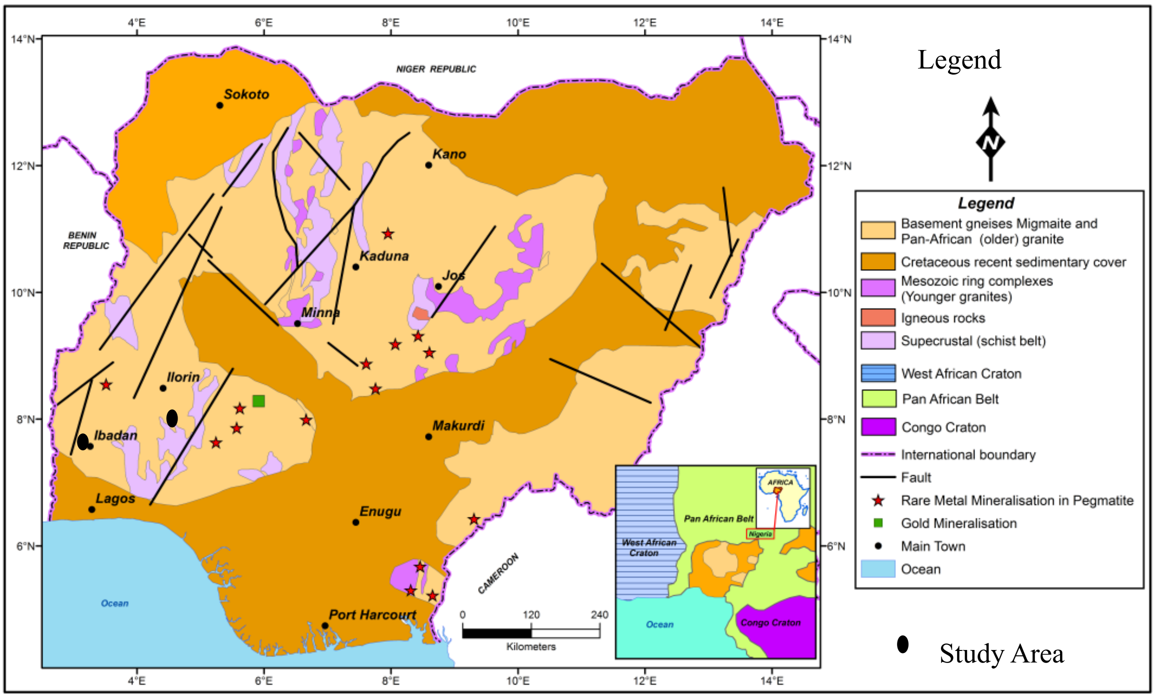


Figure 1. Map of Nigeria showing the location of the study area

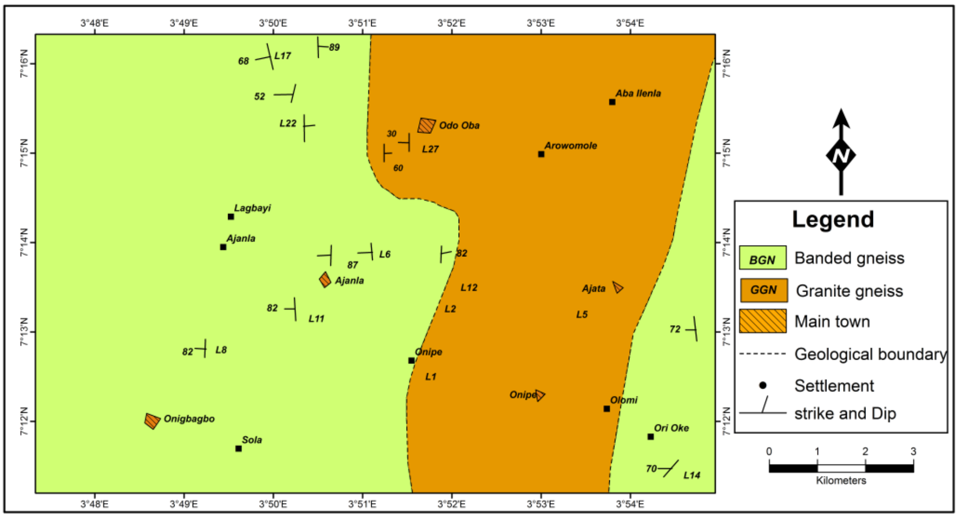


Figure 2. Geological map of Idi-Ayunre area and its' environs

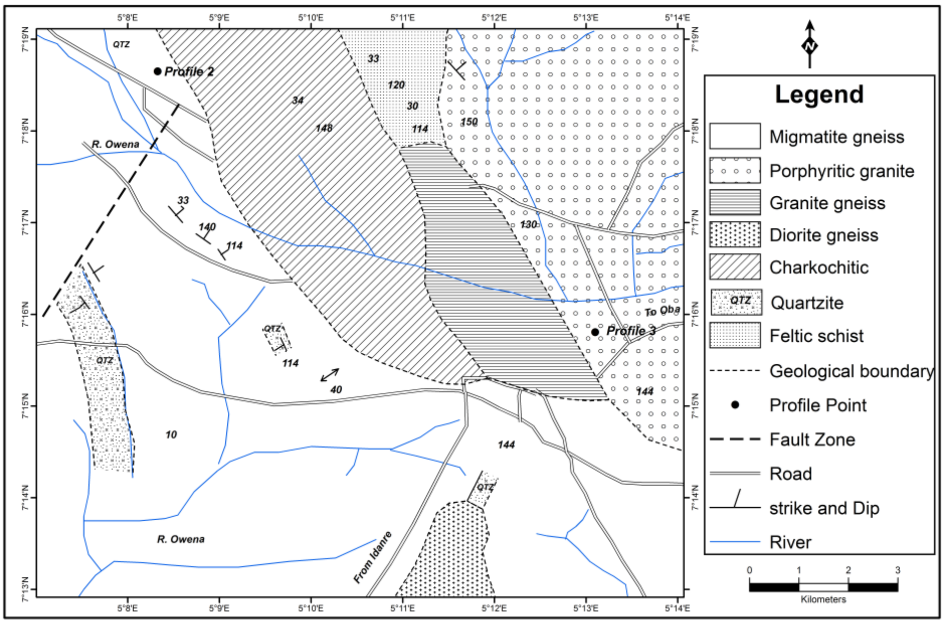


Figure 3. Geological map of Akure area showing clay sites

3. Materials and Method

Representative samples were collected from different vertical sections of the clay bodies. Clay mineralogy was determined using X-ray Diffraction (XRD) at Activation Laboratory in Canada. The X-ray diffraction analysis was performed on a Panalytical X'Pert Pro diffractometer, equipped with a Cu X-ray source and an X'celerator detector, operating at the following conditions: voltage: 40 kV; current: 40 mA; range: 5-80 deg 2θ; step size: 0.017 deg 2θ; time per step: 50.165 sec; divergence slit: fixed, angle 0.5°. The crystalline mineral phases were identified in X'Pert HighScore Plus using the PDF-4 Minerals 2013 ICDD database. The quantities of the crystalline minerals were determined using the Rietveld method. The Rietveld method is based on the calculation of the full diffraction pattern from crystal structure information.The X-ray power diffraction patterns were obtained using a Siemens. Elemental compositions of the rocks and clay samples were determined using Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). For ICP-MS, microwave high pressure/temperature decomposition of samples (230^{o}C, 7.0Mpa; Paar Physical Multiwave sample preparation system) using Merck Suprapurs grade reagents (HF, $HClO_4$, HNO_3 and HCl). All measurements were made on a Sciex/Perkin-Elmer ELAR 6000 ICP-MS. Grain size distribution data were obtained by conducting grain size analysis in two parts:

sieve analysis for coarse grained fraction, such as gravel and sand and sedimentation for silt and clay fraction , plasticity tests, density measurement, linear shrinkage and water absorption capacity of the were determined in order to assess the industrial suitability.

4. Results and Discussion

4.1 Field Work and Macro-Petrography

In Idi-Ayunre, the major clay occurrences is at the western part of town. A 7m thick profile over banded gneiss is exposed in a quarry and essentially residual. The presence of relic structures of parent rock and angular quartz grains in the profile strongly supported its *insitu* nature. Four distinct layers were identified based on color, texture, and relic structures in the saprolitic zone (Figure 4a.). The upper horizon which is the topsoil is generally light brown in color and is about 0.2m thick. It contains rootlet of plants and rich in organic matter (humus). This layer is friable and contains some pebbles of quartz. Below this layer is a reddish and partly consolidated laterite which is about 1.2m in thickness. The lateritic layer grades gradually into the underlying clayey horizon. In this layer, the organic content has almost disappeared. Underlying the laterite layer is the clayey layer which is about 3.8m thick. The clay layer is underlain by saprolitic zone which graded into the bedrock. The contact between the clayey layer and the saprolite is sharp.

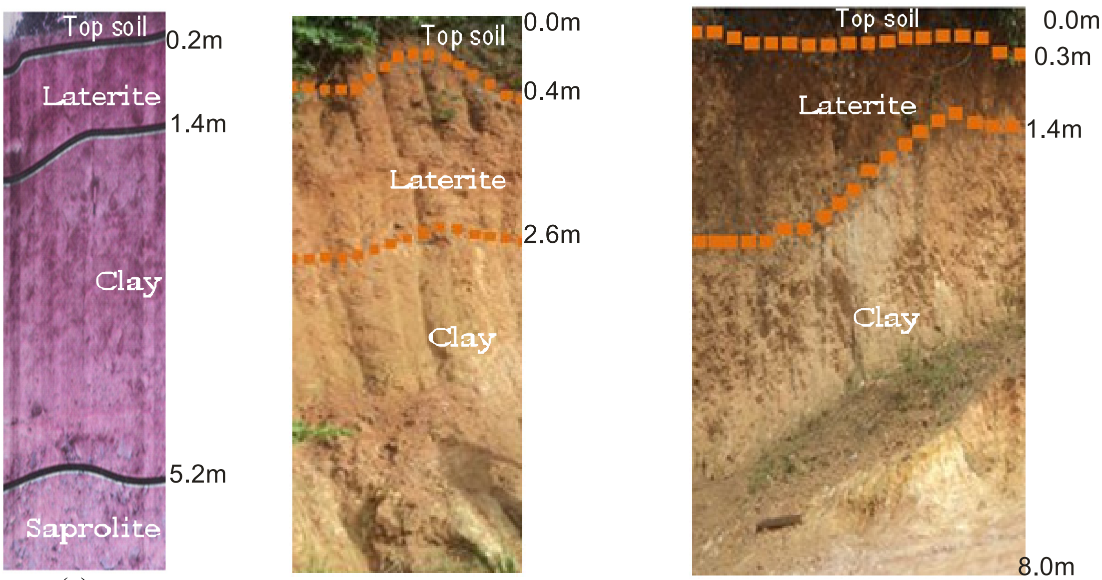


Figure 4. Weathered profiles of the study areas

(a)- Idi-Ayunre brown variety, (b)-Akure brown clay, (c)- Akure dark brown body

The main clay occurrence at Akure is behind Reighneth Filling Station, about 300m to the second gate of Federal University of Technology Akure (FUTA) (Figure 4c). A 10m thick residual profile overlies the migmatite gneiss. On the field, there is no evidence of soil movement or transportation hence it is assumed that they are *insitu*The reddish laterite which is overlain by top soil grades gradually into clay horizon which is dark brown in color with10m thickness.

The second clay occurrence is located above porphyritic granite in Akure. A 6m thick profile was exposed and consists of 4 distinct layers around Fiwasaye Girls Grammar School, Akure (Figure 4b).The weathered profile over porphyritic granite is residual. Laterite grades gradually into the clay layer which is about 3m thick. It is light brown in color, organic material in this layer has disappeared completely. The brown clay deposit in Fiwasaye area of Akure is similar to that of Idi Ayunre in field and textural characteristics.

4.2 Mineralogy

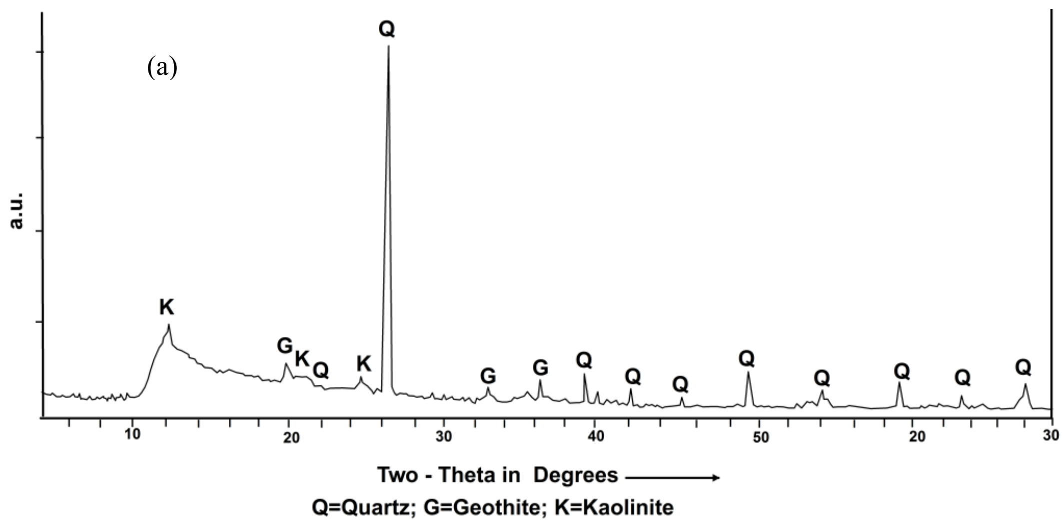
The X-ray difractograms of clays derived from weathered banded gneiss, porphyritic granite and migmatite show that kaolinite is the dominant clay mineral in the profiles. Quartz is apparently present in all the samples because of its high resistance to weathering and it's the major non-clay mineral that exhibits notable intensities in the difractograms. Distinctive peaks of kaolinite are recorded at d = ~7.14Å, d = ~4.36 Å and d = ~3.57 Å in the unoriented and non-glycolated samples (Figure5). Geothite is present only in Idi Ayunre clay with peaks at d = ~4.18Å, and d = ~2.60 Å

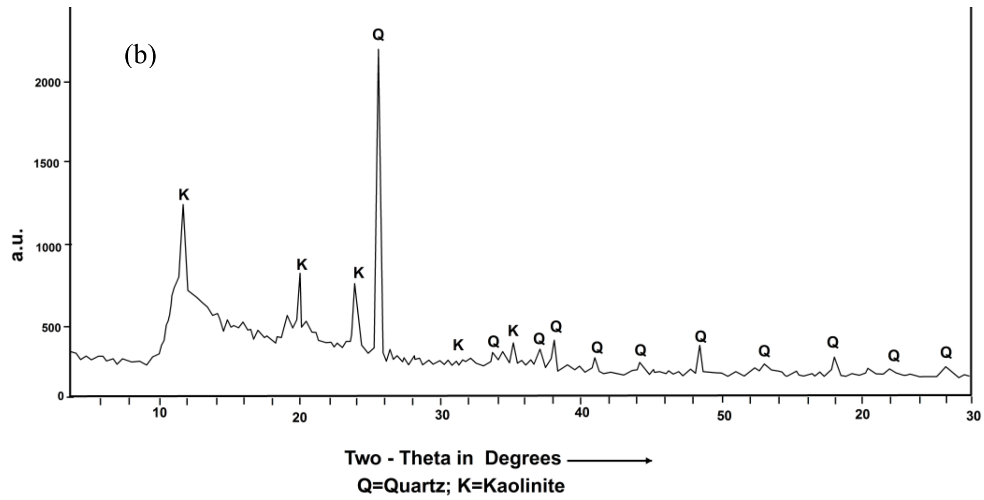
4.3 Chemical Compositions

The average concentrations of major elements in the residual clays of Idi-Ayunre and Akure are presented in Table 1. The mean compositions of SiO_2 in Idi-Ayunre and Akure clay deposits are 59.25%, 47.43% and 50.11% respectively. The silica content is relatively high in Idi-Ayunre and this is comparable to Isan (red clay) and Ara-Ijero (grey) (Bolarinwa, 1995) and that of Akure is relatively low compared to similar residual clay deposits at Ibadan (Emofurieta, 1988), Al_2O_3 content is relatively high in Akure residual clays than Idi Ayunre deposit. The high Fe_2O_3 content of about 5% in Idi-Ayunre clay is responsible for its brownish colouration. The brown derived clay on the other hand contains only 3.45% Fe_2O_3. K_2O abundances is higher Idi-Ayunre clay (3.25%) and generally low (0.04%) in Akure clays whereas concentrations of CaO, MgO and MnO are generally low and less than 0.5%. Therefore, the brown Idi-Ayunre is appreciably discriminated in CaO. Akure residual clays have higher H_2O+ than Idi-Ayunre deposits.

Major elements abundances show that the clay samples have SiO_2, (ca.52.26%), Al_2O_3 (ca. 30.29%) and Fe_2O_3 (ca3.67%) constituting more than 85% of the bulk chemical compositions. Al_2O_3 content is higher, while SiO_2, Fe_2O_3 are lower in the Akure chocolate body than others. Fe_2O_3, K_2O, MgO, CaO, Na_2O are higher in Idi-Ayunre clay samples than Akure clay.

A comparison of the chemical compositions of the clay samples with China clay (Huber, 1985) shows that the SiO_2, and Al_2O_3 values of dark brown Akure clay compared favourably, except that the Fe_2O_3 content is high. However, brown Akure clay and Idi-Ayunre clay types compared favourably with Florida active kaolinite and plastic fire clay of St. Louis (Huber, 1985). In terms of functional applications, the chemical compositions (Table 2) are within the limits of industrial specification for ceramics.





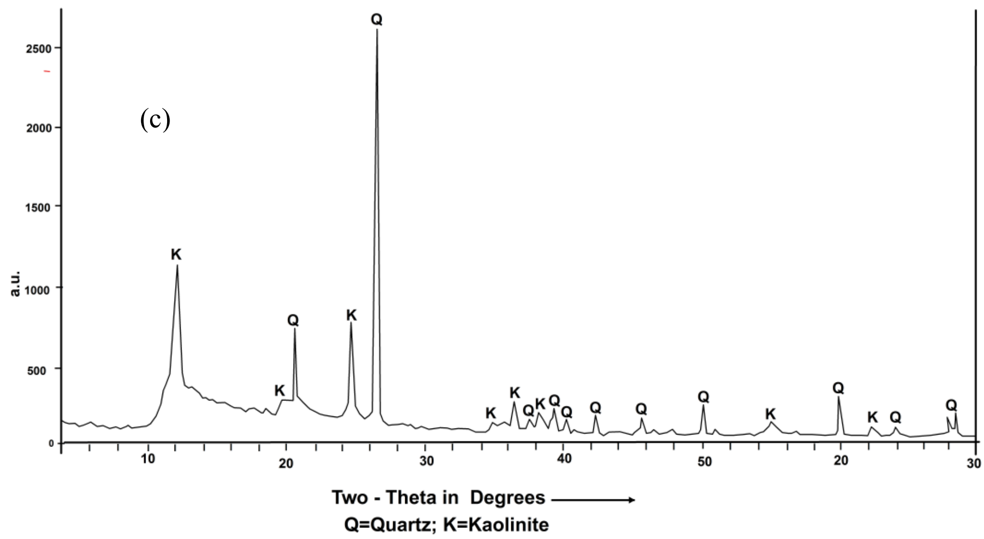


Figure 5. X-ray diffraction diagrams for the clays samples (a) -Idi-Ayunre brown variety, (b)-Akure brown clay, (c) - Akure dark brown body

(note: a.u =arbitrary unit)

Table 1. average chemical composition of Idi-Ayunre and Akure residual clays

Oxides	*Idi-Ayunre (Brown) %	*Akure- (Brown) %	*Akure- (Chocolate) %	Reference (A) %	Reference (B) %	Reference (C) %
SiO_2	59.25	50.11	47.43	52.92	57.67	46.88
Al_2O_3	22.53	32.34	36.01	9.42	24.00	37.65
Fe_2O_3	4.72	3.45	2.46	3.65	3.23	0.88
MgO	0.83	0.03	0.05	0.08	0.30	0.13
CaO	0.90	0.02	0.01	1.91	0.70	0.03
Na_2O	1.60	0.01	0.01	0.03	0.20	0.21
K_2O	3.25	0.04	0.03	0.98	0.50	1.60
P_2O_5	0.07	0.09	0.05	0.02	-	-
MnO	0.02	0.01	0.01	-	-	-
LOI	6.15	11.76	12.75	10.19	10.50	12.45
TOTAL	99.81	96.47	99.65	79.20	97.10	99.83

*Average values for 5 samples

A. Florida Active Kaolinite (Huber, 1985)

B. Plastic Fire Clay, St Louis (Huber, 1985)

C. China Clay (Huber, 1985)

Table 2. Comparison of Idiayunre and Akure clays with some industrial chemical specifications

Oxides	Idi-Ayunre (Brown) %	*Akure Brown %	*Akure Chocolate) %	Some industrial specification		
				(A) %	(B) %	(C) %
SiO_2	59.25	50.11	47.43	47.90-48.30	67.57	51.0-70.0
Al_2O_3	22.53	32.34	36.01	37.90-38.40	26.50	25.0-44.0
Fe_2O_3	4.72	3.45	2.46	13.40-13.80	0.50-1.20	0.2-0.7
MgO	0.83	0.03	0.05	0.20-0.30	0.10-0.19	0.2-0.7
CaO	0.90	0.02	0.01	0.03-0.25	0.18-0.30	0.1-0.2
Na_2O	1.60	0.01	0.01	0.20-0.35	0.20-1.50	0.8-3.5
K_2O	3.25	0.04	0.03	0.40-0.10	1.10-3.10	-
P_2O_5	0.07	0.09	0.05	0.02	-	-
MnO	0.02	0.01	0.01	-	-	-
LOI	6.15	11.76	12.75		-	-
TOTAL	99.81	96.47	99.65	-	-	-

* Average values for 5 samples

(A) - Paints (Payne, 1961)

(B) - Ceramics (Singer and Sonja, 1971)

(C) - Refractory Bricks, (Parker, 1967)

Table 3. Physical and firing properties of the Idi-Ayunre and Akure clays

Profile	Clay Fraction	Atterberg Limits		LOI (%)	LSK(%)	WAC(%)	S.G	Colour
		LL (%)	PI (%)					
* IdiAyunre clay	30	30.03	15.82	20.85*	9	4.52	2.60	Brown
*Akure brown	43	43.75	20.18	18.91	11	10.84	2.50	Brown
*Akure	37	31.02	13.78	22.35	9	10.84	2.55	Chocolate

* Average values for 5 samples

LOI – Loss on ignition

LSK – Linear Shrinkage

WAC – Water absorption capacity

LL – Liquid limit

PI – Plasticity index

S.G.- Specific Gravity

4.4 Industrial Properties

Evaluation of industrial properties such as thermal characteristics, specifically shrinkage, loss on ignition and firing colour were evaluated. The summary of the results of industrial properties are presented in Table 3. Loss on ignition vary between 18.91% and 22.25% with a mean average of 20.70%. The average values of water absoption capacities of the fired pellets from Idi-ayaunre and Akure clays after immersion in cold water for 24 hours are 4.52% and 10.84% respectively. The colour of the fired pellets ranged from brown to redish brown in consonance with the high percentage of iron compounds that are present in the samples. The linear shrinkage values range from 9% to 11% in pellets from Akure clays, while Idi-Ayunre pellets have an average value of 9%. The average specific gravity of Akure and Idi Ayunre clays are 2.50, 2.55 and 2.60 respectively.

Results of wet sieve analysis (Table 3) show that the average clay fraction of Akure brownish clay samples (43.75%) are greater than that of the Idi-Ayunre samples (30.03%), whereas the dark brown sample from Akure have average value of 31.02%. Plots of plasticity indices against the liquid limit values (Figure 6) classify Idi-Ayunre and Akure clays as an inorganic clays with moderate compressibility and moderate toughness. All the bodies posses adequate mouldability which is n estimate of their workability

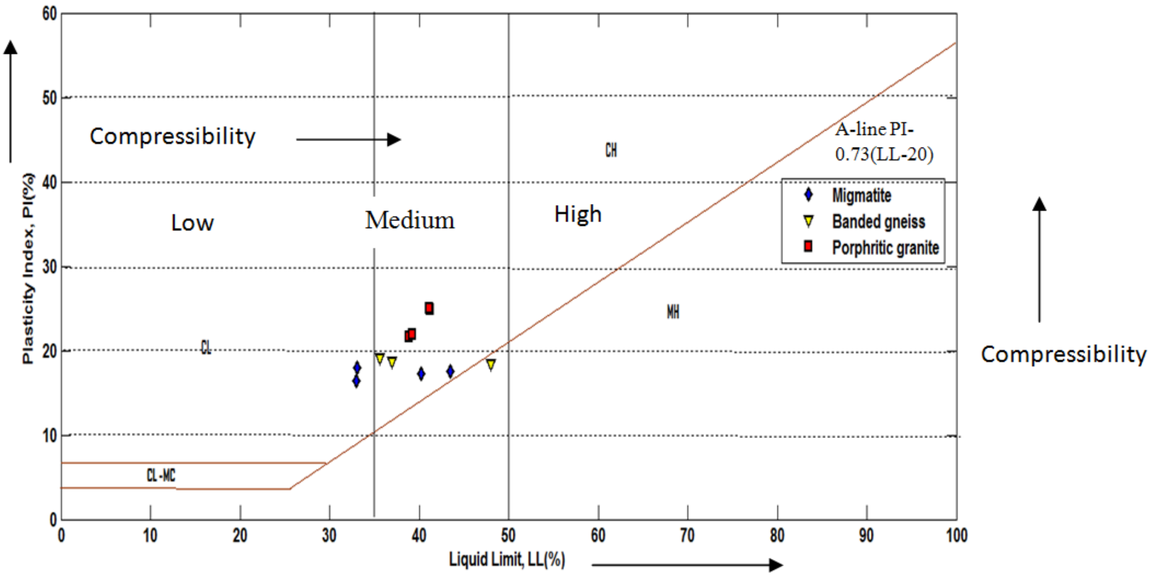


Figure 6. A plasticity chart for classification of the clay deposits (after Casagrande 1948)

5. Discussion

The data resulted from macropetrography and XRD show that the residual clay profiles developed over the basement complex in Akure and Idi-ayunre are dominantly kaolinitic. The Akure brown clay is the most plastic of the three varieties studied. Due to the greater content of fine clay size materials. Quartz and goethite are some of the impurities detected in the samples. The presence of goethite shows that the ferromagnesian minerals such as biotite has been completely weathered and converted to goethite.

Based on physical parameters, the studied clay occurrences possesses adequate mouldability, the chocolate to brown colour when fired. The linear shrinkage is relatively lower, while the water absorption capacity is lower in Idi-Ayunre clay than Akure bodies. A general assessment of the chemical, mineralogical and physical characteristics of the residual clay shows that they are amenable to beneficiation. Fe_2O_3 and other impurities can be reduced in Akure clay bodies with appropriate processing methods and this will significantly lead to the enhancement of Al_2O_3. Similarly, screening of the samples will drastically reduce the quartz content and this will reflect in the depreciation of SiO_2 abundances

The composition of the clays are quite comparable to the Florida active kaolinite, the plastic clays of St Louis (Huber, 1985). Akure and Idi-Ayunre clays would be suitable for the production of paints, rubber, paper and textile industries when further beneficiated. The Akure dark brown clay on the other hand would be adequate for the production of ceramic wares, refactories and building bricks.

On the basis of the chemical and mineralogical composition of clay raw materials, ternary diagrams have been constructed for their use in the traditional products of ceramics industry: ‘red-stoneware’, cottoforte’ and ‘majolica’ (Fabbri and Fiori 1985). This ternary diagram is the most suitable to define and visualize compositional fields. On this diagram (Figure 7), Idi Ayunre brown clay falls near the global fields ‘red-stoneware and this depicts that only Idi Ayunre brown clay is suitable for the production of red-stoneware products. These chemical compositions are similar to the clay materials from Bailen area (South Spain) and Greece (Figure 8) being used for making red stoneware (Gonzalez et al. 1997, Oikonomopoulus et al. 2007). Idi Ayunre brown clay shows a high iron content and that responsible for the brownish colour. In addition, Idi Ayunre has the highest relative amount of alkalis ($Na_2O + K_2O$), (around 4.85%) and this favourably compared with Moro and Chulilla clays employed for the production of ceramic in Castellon (Meseguer 2011).

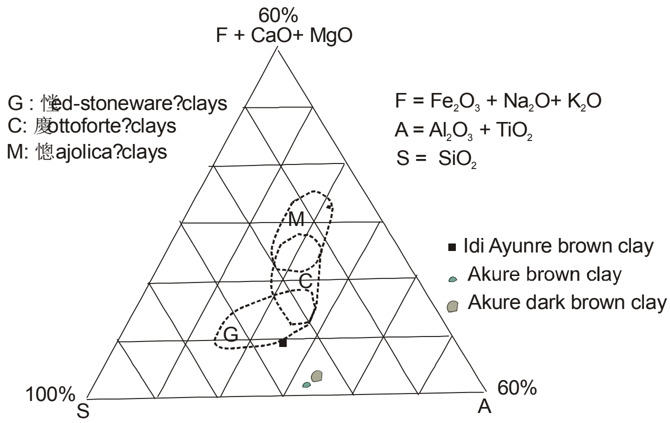


Figure 7. Ternary diagram $SiO_2/Al_2O_3+TiO_2/Fe\text{-}_2O_3$ + MgO +CaO+ K_2O + Na_2O (After Fabbri and Fiori, 1985)

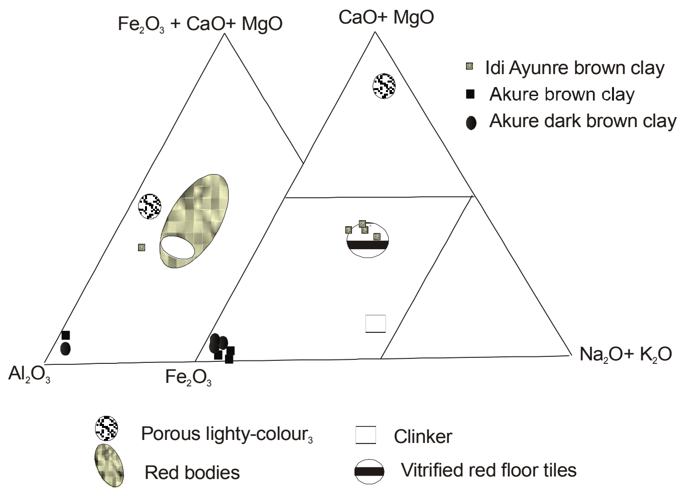


Figure 8.

Based on the field observation, the residual clay bodies show that, they occur within 1 to 3 meters to the surface and from the economic point of view the clay bodies could be profitably mined through the open pit method. Exploratory drilling would be highly recommended in follow-up investigation to accurately establish the clay reserves. In conclusion, the Idi-Ayunre and Akure clay bodies would readily provide raw materials for the production of bricks and ceramic wares with simple and effective screen

6. Conclusion

The mineralogical study of the clay materials shows that kaolinite is the dominant mineral in the of clay in the area of study. In addition to clay minerals, the other mineral phases identified are mainly quartz and goethite. From a mineralogical and chemical point of view, Idi Ayunre clay favours the production of ceramics and Akure brown clay and Akure dark brown clay would be adequate for the production of refractories and burnt bricks

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